LITERATURE CITED

- 1. N. P. Gambaryan, D. P. Del'tsova, and Z. V. Safronova, Izv. Akad. Nauk SSSR, Ser. Khim., 1814 (1987).
- 2. A. V. Fokin, A. F. Kolomiets, and N. V. Vasil'ev, Usp. Khim., 53, 416 (1984).
- 3. Yu. V. Zeifman, E. G. Ter-Gabrielyan, N. P. Gambaryan, and I. L. Knunyants, Usp. Khim., 53, 452 (1984).
- 4. N. P. Gambaryan, G. S. Kaitmazova, É. M. Kagramanova, et al., Izv. Akad. Nauk SSSR, Ser. Khim., 1102 (1984).
- 5. D. P. Del'tsova and N. P. Gambaryan, Izv. Akad. Nauk SSSR, Ser. Khim., 1367 (1984).
- 6. D. P. Del'tsova, M. P. Krasuskaya, N. P. Gambaryan, and I. L. Knunyants, Izv. Akad. Nauk SSSR, Ser. Khim., 2086 (1967).

REACTION OF POLYFLUORINATED β -KETOACID ESTERS AND THEIR α -HALO DERIVATIVES WITH PHOSPHORUS PENTACHLORIDE

UDC 542.944:547.484'161

M. B. Bobrov, V. I. Saloutin, M. I. Rudaya, and K. I. Pashkevich

Acetoacetic esters react with PCl_5 in benzene via the carbonyl as well as the ester group (6 h at 0°C and subsequent treatment with water) to give β -chlorocrotonic acid [1, 2]. When the reaction time is decreased to 2 h and the reaction is carried out in CHCl₃, a mixture (1:1) of ethyl- β -chlorocrotonate and ethyldichlorobutanoate is also isolated [3]. In this reaction methyl- α -chloroacetoacetate in CHCl₃, after treatment with methanol, affords the α,β -dichlorocrotonic ester [4].

However, no information is available about the reaction of PCl₅ with β -ketoesters.

In the present work we studied the reaction of fluoroalkyl- (I), α -chloro- (II), and α, α -dibromo- β -ketoesters (III) with PCl₅ in C₆H₆, CHCl₃, CCl₄, and POCl₃.

It was shown that compounds (I) and (II), when boiled for 6-12 h with PCl_5 in C_6H_6 , $CHCl_3$, and CCl_4 , react via carbonyl group RpCO to form fluorine-containing β -chloro- and α,β -dichlorocrotonic esters (IV) and (V), respectively (as an isomeric mixture; see Table 1). Increasing the reaction time and using excess PCl_5 have no effect on the product composition.



 $R_{F} = HCF_{2}$ (a), CF_{3} (b), $C_{4}F_{9}$ (c), $H(CF_{2})_{2}$ (d).

Using compound (VI), we showed that β -chlorocrotonic esters (IV) of the same isomeric composition are obtained in satisfactory yield when PCl₅ reacts with fluorine-containing β -ketoester copper chelates:

Institute of Chemistry, Ural Science Center, Academy of Sciences of the USSR, Sverdlovsk. Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 9, 2024-2030, September, 1987. Original article submitted February 13, 1986. TABLE 1. α , β -Unsaturated α -X- β -Fluoroalkyl β -Chlorocarbonic Acids (VII), (VIII) and Their Esters (IV), (V)

	IR spectrum ν , cm ⁻¹		PMR spectrum δ, ppm (J, Hz)			
Compound	C=0	OH br.	CH=	−с≮ ^о он	H(CF ₂) _n	
(VII _a)	1708 1712	2890 3050	6,48 6.62	11,24	7,27t (54,0) 6.11t (54,7)	
(VIIb)	1725 1720	2930 3080	6,79 5.98	9,99		
(VIIc)	1730 1728	3050 2920	$6,62 \\ 6,02$	9,58		
(VIId)	1725 1723	3050 2930	6,78 6.06	9,71	6,05 tr.t (52,8; 4,2)	
(VIIIa) (VIIIb)	1750 1750 1740	3000 3000		9,8 9,4	7,12 t (54,0)	

TABLE 2. IR and PMR Spectral Data for R_{F} -CCl=CX-CO₂H (VII), (VIII)

HCF₂ OMe $\xrightarrow{\text{PCl}_5, \text{ CCl}_4}$ (IV a) $\xrightarrow{\text{Cl}_1/2}$ (VI)

The ester groups of polyfluorinated β -ketoesters (I) and (II) react only under more drastic conditions: boiling for 36-60 h with a threefold excess of PCl₅ in POCl₃.

In this case, in addition to β -chlorocrotonic esters (IV) and (V), the corresponding acid chloranhydrides are also formed; these afford acids (VII) and (VIII) after treatment with water. The fraction of β -fluoroalkyl α , β -unsaturated β -chlorocarbonic acids (VII) in the product mixture decreases with an increase in the chain length of the fluoroalkyl substituent. Introduction of a chlorine atom in the α -position of the β -ketoester further impedes the reaction of the ester group; at $R_{\rm F} = C_4 F_9$ (IIa), the reaction does not proceed at all under the given conditions.

When the reaction time of compounds (Ia, b) with PCl_5 in $POCl_3$ is increased to 3-4 days, a side-reaction channel is opened up, and, along with compounds (IV) and (VII), products of chlorination in the α -position are formed: fluoroalkyl α , β -unsaturated α , β -dichlorocarbonic acids (VIII) (identified by NMR and GLC with the aid of known samples; Table 2).

 α, α -Dibromoacetoacetic ester does not react with PCl₅ in CCl₄ at 100°C; at higher temperatures it forms a resin, as it does in the absence of PCl₅. Fluorine-containing α, α dibromo- β -ketoacid esters (IIIb, c) react with PCl₅ only under drastic conditions (autoclave, 3 days, 200°C), forming a complex product mixture (that is difficult to identify) with a prevalence (∞ 50%) of dibromomethyl fluoroalkyl ketones (IXb, c) (identified by GLC and IR and PMR spectra with the aid of known samples).



Compounds (IXb, c) probably result from the decarboxylation of the appropriate α, α -dibromo- β -ketoacids, which are formed when the reaction mixture is treated with water. This indicates that compounds (IIIb, c) react with PCl₅ via the ester group.

Compounds (IV) and (V) may exist in four isomeric forms:



^{*}At X = Cl the given isomer designations do not conform to the IUPAC rules; we have used them only to preserve the unity of the nomenclature in comparing isomers of compounds (IV) and (V).

-										
ы 🔆	spectrum • cm-1		PMR spec	trum, δ, ppm (J, Hz)	Dipole m	oment, D		Isomer 18	atio, ϕ_{0}	
	vC=0	CH=	-OCH3	$\mathrm{H(CF_2)}_{n}$	^µ calc.	μ expt.	cis-s-cis	cis-s-trans	trans-s- trans	trans-s-cis
	1738 1732	7,42 6,57	3,82 3,80	7,44t (54,0) 6,08t (54,7)	3,07	3,09		28	42	
	1755 1720	5,80 5,63 5,45	3,83 3,81 3,81 3,80		3,24	3,02	49	41	10	
	1772 1750	6,98 6,75 5,68	3,90 8,90 85		3,32	3,39	71	18	11	
	1790 1755	$6,58 \\ 6,40 \\ 5,96 \\$	3,85 9,83 9,83 9,83 9,93 9,93 9,93 9,93 9,93	6,10tr ₄ t (52,8; 4,2) 6,17tr ₄ t (52,8; 4,2) 6,06tr ₄ t (52,8; 4,2)	2,57	2,62	20	68	12	
	1728		3,92	7,24 t (54,0)	2,24	2,36	100			
	1770 1760		3,96 9,89 9,89 9,83 9,90		2,52	2,43	73			17
	1775 1750		4,01 3,97		2,95	2,78	80			20

TABLE 3. IR and PMR Spectral Data and Dipole Moments for $\rm R_{F}-CC1=CX-CO_{2}Me~(IV)$, (V)

*The given absorption frequencies represent the aggregate absorption of each geometric isomer.

	Calculated Hypothetical isomer content of mixture, dipole mo- % by variant					
Isomer	ment of isomer, D	1	2	3	4	
cis-s-cis cis-s-trans trans-s-trans trans-s-cis Calculated dipole moment of mixture, D	3,88 1,07 0,92 4,50	71 18 11 3,32	18 71 11 1,90	$71 \\ 18 \\ -11 \\ 3,62$	$ \begin{array}{c c} 18 \\ 71 \\ \hline 11 \\ 2,40 \end{array} $	

TABLE 4. Determining the Isomeric Composition of Compound C_4F_9 -CCl=CH-CO₂Me

Thus we may anticipate the appearance of four carbonyl bands in their IR spectra. The experimental spectra of these compounds have two or three bands. Their PMR spectra have two or three sets of proton signals of methine and ester groups (Table 3), corresponding to geometric as well as conformational isomers.

Based on the data in [2, 5], we assigned the geometric isomer signals proceeding from the fact that in the PMR spectra both the methine and ester group proton signals of the cis isomer lie downfield to those of the trans isomer, whereas in the IR spectra the carbonyl group frequency of the cis isomer is greater than that of the trans isomer. However, when conformers are present in esters (IV) and (V), their assignment on the basis of IR and PMR spectra becomes difficult, since it is impossible to distinguish cisoid and transoid isomers. In these cases the isomers were identified by using a combination of spectral data and the measured dipole moments of the compounds according to the following scheme: 1) the isomer content (in %) was evaluated from the integral intensities of the signals in the PMR spectra; 2) the content (in %) of geometric isomers, i.e. % cis-s-cis and cis-s-trans and % transs-cis and trans-s-trans, was evaluated from the carbonyl band intensities in the IR spectra (see Table 3); 3) a hypothetical isomer composition was determined using the geometric isomer assignment rules [2, 5]; 4) the dipole moments of all possible isomers were calculated; from this the dipole moment of the mixture with the hypothetical isomer composition was calculated and then compared with the experimentally obtained dipole moment. The dipole moments of cisoid and transoid conformers, in cis as well as in trans isomers, differ significantly [by 3-4 D for compound (IV), and by 2-3 D for compound (V)]. Therefore, the structure of the prevalent isomer can be determined unequivocally. Thus, for example, for compound (IVc) the isomer ratio found from the signal ratio in the PMR spectra is 71, 18, and 11%. According to [2, 5], the 71% isomer should be assigned a cis configuration (methine proton signal in the weakest field), and the 11% isomer should have the trans form.

The IR spectrum shows that the mixture contains 90% of the cis isomer. Therefore, four isomer assignment variants may be inferred (Table 4). The experimentally determined dipole moment of the mixture (μ_{expt}) was 3.39 D; thus the cis-s-cis isomer is the prevalent form (71%), with the realization of variant 1. The isomeric composition of the other compounds was determined in a similar manner. The results (see Table 3) show that the cis-s-cis isomer is the prevalent form in compounds (IVb, c), which have perfluorinated substituents; the fraction of the cis-s-cis isomer increases with an increase in the R_F length. In compounds with a terminal hydrogen atom in the fluoroalkyl substituent, the cis-s-trans isomer (IVa, d) is the prevalent form (see Table 3). In compounds (V) the cis-s-cis isomer is the prevalent form regardless of the type of fluoroalkyl substituent. In nonfluorinated β -chloro-[2, 3] and α , β -dichlorocrotonic esters [4], the trans isomer is the prevalent form.

EXPERIMENTAL

IR spectra of the compounds (1% solutions in CC1₄) were recorded on an UR-20 spectrometer. PMR spectra (in CDC1₃, TMS standard) were obtained on a Tesla BS-567 A (100 MHz) instrument. GLC was carried out on a LKhM-72 chromatograph (carrier gas: helium; katharometer detector; steel column, 2 m × 4 mm, packed with 5% N-AW-DMCS, Silicone SE-30; column temperature, 150°C). Experimental dipole moments were determined in benzene at 25 ± 0.1°C on a Tangens-2M instrument at a frequency of 1 MHz. In calculating dipole moments according to the vector scheme, group dipole moment values were used [7]. Fluoroalkyl α -chloro- and α,α -dibromo- β -ketoesters (II) and (III) were obtained according to [8]; dibromomethyl fluoroalkyl ketones (IX) were obtained according to [9]. 6,6-Dibromo-1,1,1,2,2,3,3,4,4-nonafluorohexanone-5 (IXc). Yield, 70%; bp, 60°C (20 mm). Found (%): C 17.10, H 0.43, Br 38.0, F 40.3 (C₆HBr₂F₉O); Calculated (%): C 17.12, H 0.24, Br 37.97, F 40.86. IR spectrum (ν, cm⁻¹): 1770 (C=O). PMR spectrum (δ, ppm): 6.25 s (1H, CHBr₂).

<u>β-Fluoroalkyl α,β -Unsaturated α -X- β -Chlorocarbonic Acid Esters (X = H, Cl) (IV), (V).</u> An 11.5-g (55 mmole) portion of PCl₅ in 100 ml CCl₄ was placed in a flask fitted with a mixer and a reflux condenser. The mixture was heated to boiling, with mixing, and after 0.5 h 50 mmoles of β -ketoester (I), (II) was added dropwise. The mixture was boiled, with mixing, for 6-12 h. It was then cooled and poured over crushed ice. The organic layer was washed with water, saturated Na₂CO₃ solution, then again with water (alkaline medium), and then with saturated NaCl solution. The material was dried over MgSO₄, the CCl₄ was evaporated, and esters (IV), (V) were distilled (see Table 1).

A 50-mmole portion of β -ketoester (VI) copper chelate in 200 ml CCl₄ was placed in a flask fitted with a mixer and reflux condenser; the solution was heated to boiling. After 0.5 h, finely ground PCl₅ (75 mmoles) was added. The mixture was boiled, with mixing, for 6 h, then cooled, and filtered to remove CuCl₂. The filtrate was poured over ice and treated as described above.

Fluoroalkyl α,β -Unsaturated α -X- β -Chlorocarbonic acids (VII), (VIII). A 150-mmole portion of PCl₅ in 100 ml CCl₄ was placed in a flask fitted with a mixer and a reflux condenser; the mixture was heated to boiling, with mixing. After 0.5 h, 50 mmoles of β -ketoester (I), (II) was added dropwise, and boiling continued for 36-48 h. The mixture then was cooled, poured over crushed ice, and extracted with chloroform. The organic layer was separated, extracted with saturated Na₂CO₃ solution, and washed with water and saturated NaCl solution. Esters (IV), (V) were obtained as described above. The soda extract was acidified to a weakly acid pH and extracted twice with ether. The pooled ether extract was dried over MgSO₄, the ether was evaporated, and acids (VII), (VIII) were distilled (see Table 1).

<u>Reaction of Fluoroalkyl α, α -Dibromo- β -ketoester (II) with PCl₅. A mixture of 50 mmoles of compound (III) and 150 mmoles of finely ground PCl₅ in 100 ml CCl₄ was placed in a 500-ml steel autoclave and heated for 3 days at 200 °C. The autoclave contents were poured over ice and then washed with saturated Na₂CO₃ solution, water, and saturated NaCl solution. The material was dried over MgSO₄ and evaporated. Fluoroalkyl dibromomethyl ketones (IX) were identified by GLC and by IR and PMR spectra (by comparison with known samples).</u>

CONCLUSIONS

1. Fluorine-containing β -ketoesters and their α -chloro derivatives form fluorinated β -chloro- and α,β -dichlorocrotonic esters, respectively, when boiled with PCl₅ in benzene, chloroform, and carbon tetrachloride. In POCl₃ the ester group also participates in the reaction. In this case the fluoroalkyl β -ketoesters are chlorinated in the α -position.

2. At 200°C α , α -dibromo- β -ketoesters react with PCl₅ via the ester group to form dibromo-methyl fluoroalkyl ketones.

3. Fluorine-containing β -chlorocrotonic esters with perfluorinated substituents exist primarily as cis-s-cis isomers. The presence of a terminal hydrogen in the fluorinated substituent leads to a prevalence of the cis-s-trans isomer. The cis-s-cis isomer is the prevalent form in fluorine-containing α , β -dichlorocrotonic esters.

LITERATURE CITED

- 1. W. Autenreith, Chem. Ber., 20, 1531 (1887).
- 2. D. E. Jones, R. O. Morris, C. A. Vernon, and R. F. M. White, J. Chem. Soc., 2349 (1960).
- 3. R. E. Conrow and J. A. Marshall, Synth. Commun., <u>11</u>, 419 (1981).
- 4. J. G. Bauman, R. C. Hawley, and H. Rapoport, J. Org. Chem., 49, 3791 (1984).
- 5. J. S. Pizey and W. E. Truce, J. Chem. Soc., 865 (1964).
- 6. E. A. Guggenheim and V. W. Smith, Trans. Faraday Soc., 45, 714 (1949).
- 7. V. I. Minkin, O. A. Osipov, and Yu. A. Zhdanov, Dipole Moments in Organic Chemistry [in Russian], Khimiya, Moscow (1968), pp. 77-79.
- 8. V. I. Saloutin, Z. É. Skryabina, M. N. Rudaya, and K. I. Pashkevich, Izv. Akad. Nauk SSSR, Ser. Khim., 1106 (1984).
- 9. E. T. McBee and T. M. Burton, J. Am. Chem. Soc., 74, 3902 (1952).